

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
21 May 2004 (21.05.2004)

PCT

(10) International Publication Number
WO 2004/042120 A1

(51) International Patent Classification⁷: **C25C 7/02**,
1/16, C25B 9/02

[FI/FI]; Peräläntie 24 as.11, FIN-29600 Noormarkku (FI).
POLVI, Veikko [FI/FI]; Huvisuulintie 4, FIN-28200 Pori
(FI).

(21) International Application Number:
PCT/FI2003/000828

(74) Agent: **OUTOKUMPU OYJ, INTELLECTUAL
PROPERTY MANAGEMENT**; P.O.Box 27, FIN-02201
Espoo (FI).

(22) International Filing Date:
6 November 2003 (06.11.2003)

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE,
GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,
MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT,
RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: Finnish

(26) Publication Language: English

(30) Priority Data:
20021992 7 November 2002 (07.11.2002) FI

(71) Applicant (*for all designated States except US*): **OUT-
OKUMPU OYJ** [FI/FI]; Riihitontuntie 7, FIN-02200 Es-
poo (FI).

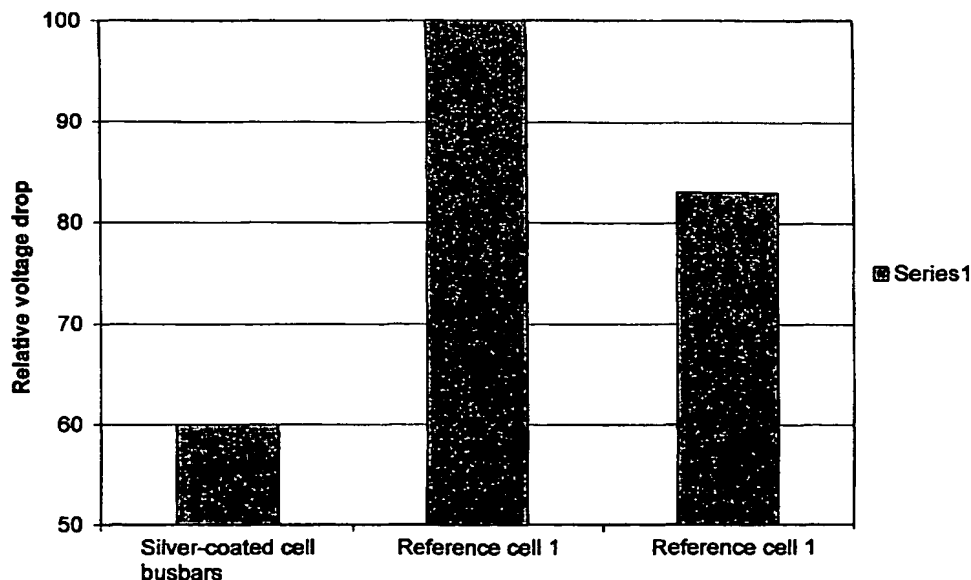
(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **OSARA, Karri**

[Continued on next page]

(54) Title: METHOD FOR OBTAINING A GOOD CONTACT SURFACE ON AN ELECTROLYSIS CELL BUSBAR AND BUS-
BAR



(57) Abstract: The invention relates to a method for forming a good contact surface on an electrolysis cell busbar used in the elec-
trolysis of metals. The contact surface of the busbar i.e. the surface onto which the support bar or lug of the electrode to be immersed
in the cell is lowered, is coated with a highly electroconductive metal. The invention also relates to an electrolysis cell busbar, on
the surface of which a highly electroconductive coating is formed.

BEST AVAILABLE COPY

WO 2004/042120 A1

**Declarations under Rule 4.17:**

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU,

TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

METHOD FOR OBTAINING A GOOD CONTACT SURFACE ON AN ELECTROLYSIS CELL BUSBAR AND BUSBAR

The invention relates to a method for forming a good contact surface on an electrolysis cell busbar used in the electrolysis of metals. The contact surface of the busbar i.e. the surface onto which the support bar or lug of the electrode to be immersed in the cell is lowered, is coated with a highly electroconductive metal. The invention also relates to an electrolysis cell busbar, on the surface of which a highly electroconductive coating is formed.

10

The fabrication of many metals such as copper, zinc and nickel, includes an electrolytic stage when the pure metal to be produced is deposited onto a cathode using an electric current, leaving the impurities in the solution. Electrolytic recovery is carried out for instance in electrolysis cells filled with an electrolyte containing sulphuric acid and electrodes (anodes and cathodes) made of electroconductive material are immersed in turn in the electrolyte. The electrode is suspended in the electrolysis cell by means of support bars or lugs, which are supported on the edges of the cell.

Electrolysis cells are connected in groups in series so that the anode of the previous cell is connected electrically to the cathode of the next cell by a busbar on top of the wall between the cells. The busbar is generally made of copper or at least copper-coated. The construction also typically includes a notched insulating bracket that goes on top of the busbar, which separates the cathode of the preceding cell from the anode busbar of the following cell. One end of the electrode support bar is placed on top of the busbar and the other usually on top of the insulating bracket. The metal to be produced is brought to the process either as a soluble anode, termed an active anode (electrorefining), or the metal is dissolved in the electrolyte, in which case the anodes are insoluble or passive anodes (electrowinning).

30

The geometry of a busbar may vary. An continuous busbar triangular in cross-section is described for instance in US patent 3,682,809. In other cases, the placing of electrodes in the cell is arranged by means of the design of the busbar. This kind of busbar is presented e.g. in US patent
5 4,035,280, where the electrodes are placed on bevelled grooves on the edges of the busbar.

US-patent 6,342,136, on the other hand, describes a main busbar that is continuous in the longitudinal direction, and equipped with protrusions of
10 different heights, between which an insulating profile is placed. One end of the cathode support bar is placed on top of the main busbar and the other end is set on top of a copper potential balancing bar, which is on top of an insulating profile. When the busbar is continuous, the support bars or lugs of the electrodes can be set down on top of the desired point of the bar. In this
15 way the whole busbar can act as the contact surface for the support bar or lug. If the busbar is notched or otherwise shaped so that the positions of the electrodes are determined, the notches or shaped points act as the contact surface of the bar.

20 The rapid wear of the contact surface is a problem with copper busbars. This is mainly due to the oxidation of copper into oxide and the corrosion of oxide into copper sulphate under the effect of the electrolyte. Copper sulphate formed on the contact surface further weakens the electrical conductivity of the busbar and in addition, the copper sulphate dissolves into the electrolyte.
25 Oxidation brings about an increase in voltage drop, because the electrical conductivity of copper oxide is significantly weaker than that of pure copper. In addition, the copper dissolving from the busbar in zinc electrolysis for example raises the copper level in the cathode zinc unnecessarily.

30 Now a method has been developed, which relates to the attainment of a good contact surface on an electrolysis cell busbar used in the electrolysis of metals, where at least the surface part of the bar is made of copper.

According to the method now developed, the area of the busbar onto which the electrode is lowered, the contact surface, is coated with a highly electroconductive metal or metal alloy such as silver or silver alloy. The copper and silver are attached to each other by means of a transmission
5 layer. When a metallic joint is formed between the transmission layer formed on the copper of the busbar and coating material, the problems caused by wear or oxidation of the lower surface of the contact piece are avoided. The invention also relates to a busbar fabricated by means of the method, for use in electrolysis cells in the electrolysis of metals, where at least the point
10 which comes into contact with the electrodes, the contact surface, is formed of a highly electroconductive layer. When the term busbar is used in the text, it also means a potential balancing bar mentioned in the prior art.

The features presented in the claims are characteristic of the invention.

15

It is important that the contact surface in the busbar conducts electricity well. The use of a highly electroconductive metal such as silver or silver alloy as coating material ensures an effective feed of current from the busbar to the electrode. The metallurgical principle for the use of silver is that although it
20 forms oxides on the surface, at relatively low temperatures the oxides are no longer stable and decompose back to the metallic form. For the above reasons oxide films do not form on the silver plating made on contact surfaces of a busbar in the same way as they do for example on a copper surface. Coating helps ensure that the electrical quality level of electrolysis
25 also remains high for long periods of time.

Silver does not form a metallurgical, very adhesive joint directly on top of copper, so instead a thin transmission layer has to be formed on the copper first, preferably one of tin or a tin-dominant alloy. Hereafter in the text for the
30 sake of simplicity we shall refer only to tin, but the term also covers tin-dominant alloys. Tin layers can be formed in many ways as beforehand by tin coating through heating, electrolytic coating or by thermal spraying

directly on the surface point before the actual coating. After this, the tin surface can be coated with silver or silver alloy. The coating with silver of the copper contact surface of the busbar can be carried out advantageously for instance with thermal spraying or soldering technique.

5

Oxidations are removed from the section of the busbar acting as contact surface before the coating is formed. It is advantageous to carry out the procedure on new bars too, but particularly when the method is applied to improve the electrical conductivity of used bars, the removal of oxidation is
10 necessary. Removal can be done for instance by sandblasting.

15

The method of coating busbars depends to some extent on the geometry of the bar. When the busbar or potential balancing bar is continuous in the longitudinal direction, coating is applied along the whole length of the bar and in that case it is preferable to do the coating by means of thermal spraying
15 technique, although of course soldering technique can also be used. If notches or grooves have been formed on the busbar as contact surfaces for the electrodes, it is naturally not worth coating areas other than these contact surfaces. In these cases too, soldering technique is an advantageous
20 method of forming the coating.

25

Thermal spraying technique can be used to coat the busbar with silver, since the melting point of silver is 960°C. An AgCu alloy can also be used as coating material e.g. in the form of wire or powder. The melting point of
25 eutectic AgCu alloy is even lower than that of silver and therefore is suitable for contact surface coating with the technique in question.

30

Out of the thermal spraying techniques available, in practice at least the techniques based on gas combustion have proved practicable. Of these,
30 High Velocity Oxy-Fuel (HVOF) spraying is based on the continuous combustion at high pressure of fuel gas or liquid and oxygen occurring in the combustion chamber of the spray gun and the generation of a fast gas flow

with the spray gun. The coating material is fed into the gun nozzle most often axially in powder form using a carrier gas. The powder particles heat up in the nozzle and attain a very high kinetic speed (several hundreds of metres per second) and are directed onto the piece to be coated.

5

In ordinary flame spraying, as the mixture of fuel gas and oxygen burns it melts the coating material, which is in wire or powder form. Acetylene is generally used as fuel gas due to its extremely hot flame. The coating material wire is fed through the wire nozzle with a feed device using a compressed air turbine or electric motor. The gas flame burning in front of the wire nozzle melts the end of the wire and the melt is blown using compressed air as a metallic mist onto the piece to be coated. The particle speed is in the order of 100 m/s.

15 Thermal spraying technique melts the surface material and since the molten droplets of the silver-bearing coating have a high temperature, a metallurgical bond is generated between the copper, tin and coating material in the coating of the contact surface of the busbar. Thus the electrical conductivity of the joint is good. The metal joining method gives rise to a eutectic of the ternary alloy of silver, tin and copper in the joint area e.g. in a temperature range of 380 – 600°C. If necessary, separate heat treatment can be carried out after spraying, which promotes the formation of a metallurgical joint.

25 When soldering technique is used to form a coating on the contact surface of the busbar, the surface to be treated is cleaned and a tin layer is formed on it, preferably less than 50 µm thick. Then the silver coating is carried out with some suitable burner. The tin layer melts and when the coating sheet is placed on top of the molten tin, it is easy to position in the correct place.

30

The method also relates to a busbar or potential compensating rail used in an electrolysis cell. A highly electroconductive layer is formed on the copper

surfaces of the busbar, particularly on those contact surfaces, which come into contact with the electrode support bar or lug. For a highly electroconductive metal or metal alloy, silver is used, or a silver alloy such as silver copper. The coating of the contact surface is preferably carried out e.g.
5 by soldering or thermal spraying technique, where a metallurgical joint is formed between the contact surface and the coating. If the busbar is longitudinally continuous, it is preferable to coat it along the whole length of the busbar. If contact surfaces are made on the bar with notches or grooves for electrodes, then only these contact surfaces are coated according to the
10 invention.

The method according to the invention is described further with the following example and the attached Figure 1,
which shows the relative voltage drops in both an electrolysis cell busbar
15 according to the invention and in reference bars.

Example

Three electrolysis cells in copper electrolysis (electrorefining) each had 81 electrodes, of which the contact surfaces coming to the busbar were
20 conventionally made of copper. One of the cells was equipped with an embodiment of the present invention, where the contact surface of the cell busbars was coated with silver. The other two cells had normal copper busbars. Figure 1 shows that the voltage drop of the silver-coated bars is much smaller than that of the conventional busbars. The voltage drop is
25 calculated as an average of the electrodes. The worst cell busbar voltage drop is taken as the value of 100 and the voltage drop of the busbars in the other cells is reported in relation to this.

PATENT CLAIMS

1. A method for forming a good contact surface on an electrolysis cell busbar used in the electrolysis of metals, where at least the surface of the bar is made of copper and the contact surface forms of an area on to which an electrode is lowered, **characterised in that** a transmission layer is formed on the copper contact surface of said busbar, after which the contact surface is coated with a highly electroconductive metal or metal alloy, wherein the coating material forms a metallurgical joint with the copper and the transmission layer.
2. A method according to claim 1, **characterised in that** the transmission layer is of tin or a tin-dominant alloy.
3. A method according to claim 1 or 2, **characterised in that** the highly electroconductive coating layer is silver.
4. A method according to claim 1 or 2, **characterised in that** the highly electroconductive coating layer is a silver-copper alloy.
5. A method according to any of the above claims, **characterised in that** in addition to a busbar the electrolysis cell is equipped with a potential balancing bar, on which a transmission layer is formed on the copper surface that comes into contact with the electrode, after which the contact surface is coated with a highly electroconductive metal or metal alloy, wherein the coating material forms a metallurgical joint with the copper and the transmission layer.
6. A method according to any of the above claims, **characterised in that** the busbar is continuous in the longitudinal direction, so that the coating layer is formed along the whole length of the busbar.

7. A method according to any of the above claims, **characterised in that** the contact surfaces of the busbar onto which the electrode is lowered, are formed by notching or grooving, wherein the coating layer is formed on the notched or grooved areas of the busbar.
- 5
8. A method according to any of the above claims, **characterised in that** the highly electroconductive coating layer is formed using soldering technique.
- 10
9. A method according to any of claims 1 - 7, **characterised in that** the highly electroconductive coating layer is formed using thermal spraying technique.
- 15
10. A method according to claim 9, **characterised in that** the thermal spraying technique is based on gas combustion.
11. A method according to claim 9 or 10, **characterised in that** the thermal spraying technique is high velocity oxy-fuel spraying.
- 20
12. A method according to any of the above claims, **characterised in that** the highly electroconductive coating material is in powder form.
13. A method according to claim 9 or 10, **characterised in that** the thermal spraying technique is flame spraying.
- 25
14. A method according to any of claims 1 – 11 or 13, **characterised in that** the highly electroconductive coating material is in wire form.
15. A method according to any of the above claims, **characterised in that** the contact surface is subjected to heat treatment after coating.
- 30

16. An electrolysis cell busbar for use in the electrolysis of metals, whereby at least a surface section of the bar is made of copper and a contact surface forms an area onto which an electrode is lowered, **characterised in that** a transmission layer is formed on the contact surface of the busbar, after which the contact surface is coated with a highly electroconductive metal or metal alloy, wherein the copper, transmission layer and coating material have formed a metallurgical joint.
17. A busbar according to claim 16, **characterised in that** the transmission layer is tin or a tin-dominant alloy.
18. A busbar according to claim 16 or 17, **characterised in that** the highly electroconductive coating layer is silver.
19. A busbar according to claim 16 or 17, **characterised in that** the highly electroconductive coating layer is a silver-copper alloy.
20. A busbar according to any of claims 16 - 19, **characterised in that** the highly electroconductive coating layer is formed using soldering technique.
21. A busbar according to any of claims 16 - 19, **characterised in that** the highly electroconductive coating layer is formed using thermal spraying technique.
22. A busbar according to any of claims 16 - 21, **characterised in that** the busbar is continuous in the longitudinal direction, wherein the coating layer is formed along the whole length of the busbar.
23. A busbar according to any of claims 16 - 21, **characterised in that** the busbar contact surfaces onto which the electrode is lowered, are

fabricated by notching or grooving, wherein the coating layer is formed on the notched or grooved areas of the busbar.

- 5 24. A busbar according to any of claims 16 - 21, characterised in that the bar is a potential balancing bar.

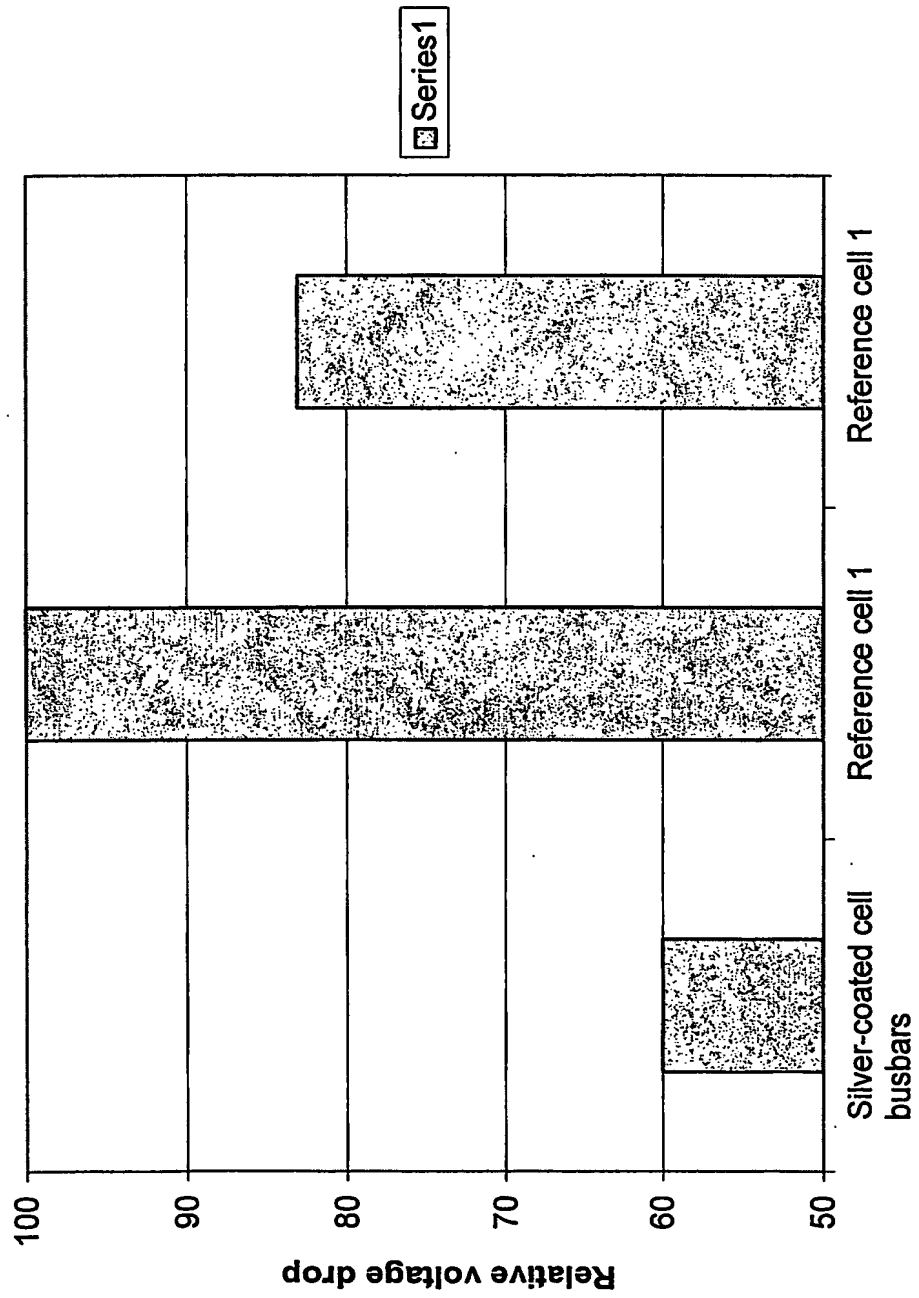


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2003/000828

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C25C 7/02, C25C 1/16, C25B 9/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C23C, C25B, C25C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6045669 A (SHINGO MATSUMOTO ET AL), 4 April 2000 (04.04.2000), column 3, line 29 - line 34, figure 1, abstract --	1-24
Y	US 4015099 A (WILLIAM SENIUK ET AL), 29 March 1977 (29.03.1977), figure 4, claim 1, abstract --	1-24
A	US 2790656 A (L.A. COOK), 30 April 1957 (30.04.1957), column 3, line 56 - column 4, line 41 --	1-24
A	US 4035280 A (RICHARD DEANE ET AL), 12 July 1977 (12.07.1977), abstract --	1-24

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 February 2004

Date of mailing of the international search report

2.7 -02- 2004

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Anna-Maj Magnusson/MP
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2003/000828

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0376447 A1 (ZIMCO INDUSTRIES (PROPRIETARY) LIMITED), 4 July 1990 (04.07.1990), abstract --	1-24
A	DE 3323516 A1 (HAPAG-LLOYD WERFT GMBH), 9 August 1984 (09.08.1984), abstract --	1-24
A	GB 2252569 A (BICC PUBLIC LIMITED COMPANY), 12 August 1992 (12.08.1992), abstract -- -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

24/12/2003

International application No.

PCT/FI 2003/000828

US	6045669	A	04/04/2000	JP	3160556 B	25/04/2001
				JP	11012779 A	19/01/1999

US	4015099	A	29/03/1977	AU	7773675 A	05/08/1976
				BE	828189 A	18/08/1975
				CA	1018477 A	04/10/1977
				DE	2506285 A,B,C	06/11/1975
				ES	434633 A	01/02/1977
				FI	60246 B,C	31/08/1981
				FI	750494 A	30/10/1975
				JP	976756 C	30/10/1979
				JP	50141520 A	14/11/1975
				JP	54007603 B	09/04/1979
				NL	165228 B,C	15/10/1980
				NL	7503125 A	31/10/1975
				NO	751509 A	30/10/1975
				ZA	7500576 A	28/01/1976

US	2790656	A	30/04/1957	NONE		

US	4035280	A	12/07/1977	AU	8691875 A	02/06/1977
				BE	836102 A	16/03/1976
				BG	39114 A	15/04/1986
				CA	1034533 A	11/07/1978
				DE	2553032 A,B,C	10/06/1976
				ES	442975 A	16/04/1977
				FI	58356 B,C	30/09/1980
				FI	753270 A	29/05/1976
				FR	2292779 A,B	25/06/1976
				GB	1490309 A	02/11/1977
				IT	1056286 B	30/01/1982
				JP	1084958 C	25/02/1982
				JP	51077503 A	05/07/1976
				JP	56025277 B	11/06/1981
				MX	3226 E	28/07/1980
				NL	169351 C	01/07/1982
				NL	7513406 A	01/06/1976
				NO	142179 B,C	31/03/1980
				NO	753835 A	31/05/1976
				PL	107694 B	29/02/1980
				TR	18566 A	11/04/1977
				YU	39753 B	30/04/1985
				YU	300375 A	30/06/1982

EP	0376447	A1	04/07/1990	AU	4385689 A	03/05/1990
				CA	2001533 A	30/04/1990
				ZA	8908119 A	25/07/1990

DE	3323516	A1	09/08/1984	NONE		

INTERNATIONAL SEARCH REPORT

Information on patent family members

24/12/2003

International application No.

PCT/FI 2003/000828

GB	2252569	A	12/08/1992	AU	1038092	A	13/08/1992
				FR	2672439	A	07/08/1992
				GB	9102562	D	00/00/0000
				GB	9202213	D	00/00/0000
				IT	1254297	B	14/09/1995
				IT	RM920078	D	00/00/0000
				ZA	9200519	A	30/12/1992

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☒ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.